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Effluent organic matter removal from reverse osmosis feed by granular activated carbon and purolite A502PS fluidized beds

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ABSTRACT

Applying pre-treatments to remove dissolved organic matter from reverse osmosis (RO) feed can help to reduce organic fouling of the RO membrane. In this study the performance of granular activated carbon (GAC), a popular adsorbent, and purolite A502PS, an anion exchange resin, in removing effluent organic matter (EfOM) from RO feed collected from a water reclamation plant located at Sydney Olympic Park, Australia were evaluated and compared through adsorption equilibrium, kinetics and fluidized bed experiments. The maximum adsorption capacity (Q_{max}) of GAC calculated from the Langmuir model with RO feed was 13.4 mg/g GAC. The operational conditions of fluidized bed columns packed with GAC and purolite A502PS strongly affected the removal of EfOM. GAC fluidized bed with a bed height of 10 cm and fluidization velocity of 5.7 m/h removed more than 80% of dissolved organic carbon (DOC) during a 7 h experiment. The average DOC removal was 60% when the bed height was reduced to 7 cm. When comparing GAC with purolite A502PS, more of the later was required to remove the same amount of DOC. The poorer performance of purolite A502PS can be explained by the competition provided by other inorganic anions present in RO feed. A plug flow model can be used to predict the impact of the amount of adsorbent and of the flow rate on removal of organic matter from the fluidized bed column.

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1. Introduction

Clean water consumption is expected to increase throughout the world in the near future with increasing demand from domestic and industrial users [1]. Unusual drought conditions are also increasing water storage requirements. An imbalance between the quantity of clean water available and the demand is leading to the alternative of manufactured water. This situation is currently critical in many countries such as Singapore and Australia. Water reclamation plants are widely implemented in these countries [2] especially reverse osmosis (RO) units which are becoming popular due to their efficient and high removal efficiency.

In many water reclamation plants, biological treated sewage effluent (BTSE) is used as the RO feed. The EfOM present in BTSE often has a low concentration but it can lead to organic and biofouling of the RO membrane [3–6]. Membrane fouling is a significant problem in RO applications because it leads to more energy consumption, frequent chemical cleaning and shorter membrane life. This ultimately increases plant treatment costs. Pre-treatment of the feed water is considered to be the most promising solution for controlling the fouling due to its simple and easy implementation. Our recent study with seawater [7] shows that a submerged membrane coagulation–adsorption hybrid system (SMCAHS) can be used for pre-treatment of seawater RO. This pre-treatment removed only 48% of DOC from seawater (DOC of 2.4 mg/L) but it helped to reduce the deposition of low molecular weight organic matter (185 Da and 90 Da) on the RO membrane. In turn this decreased initial biomass accumulation (from 4.10E08 cells/cm^2 with raw seawater to 2.75E08 cells/cm^2 with seawater pre-treated by SMCAHS).

Adsorption by GAC is often the best and most economical advanced technology for removing organic compounds from wastewater [8]. GAC adsorption proved to be effective in removing total organic carbon (TOC) from low strength synthetic wastewater [9]. According to Gur-Reznik et al. [10], GAC pre-treatments in pilot scale columns resulted in 80–90% dissolved organic matter (DOM) removal from membrane bioreactor (MBR) effluents, which in turn stabilized membrane

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permeability and increased permeate quality. Kim et al. [11] tested GAC adsorption in combination with dual media filtration (sand and anthracite) to remove organic compounds from secondary effluent. They reported that TOC removal was between 75 and 90%.

BTSE contains a significant portion of hydrophilic organic compounds and these compounds are highly ionized, so they can be removed by ion exchange [12]. A number of studies show that TOC reduction is significant when natural surface water is treated with conventional ion-exchange technology. Furthermore removing organic matter depends not only on the type of resin, but also on the DOM structure and mixture composition [13–15]. Magnetic ion exchange (MIEX) resin can effectively remove 70% of hydrophilic compounds and 55% of hydrophobic components within a very short contact time of 20 min [16]. During the ion exchange process in up-flow mode, a certain feed flow velocity can fluidize the resins and also help remove organic matter effectively. A fluidized bed packed with purolite A500PS was able to remove more than 80% DOC consistently in 8 h (more than 800 bed volumes) using 10 mg DOC/L of synthetic wastewater [17].

Many previous studies report that organic removal from synthetic wastewater by either anion exchange resins or GAC. Anion exchange resins could also remove other anions (sulphate, nitrate, etc.) from wastewater. Johir et al. [18] reported that purolite A500PS could remove more than 90% of nitrate from MBR effluents. Wang et al. [19] also showed that the presence of sulphate and nitrate in the feed solution reduced DOM removal efficiency of magnetic anion exchange resins due to the competitive adsorption. However, the removal of organics by purolite A502PS (a later version of purolite A500PS) from RO feed which contains high amount of other anions has not been reported yet. As such in this study, the removal of DOC from actual RO feed by GAC and by purolite A502PS was evaluated with real RO feed. The impact of competitive adsorption of other anions (sulphate, nitrate) by purolite A502PS was also considered. In addition, this study was carried out with both GAC and purolite A502PS using the same experimental conditions so the performance of these two can be compared in detail.

The performance of GAC and purolite A502PS was firstly evaluated by isotherm and kinetic experiments. The fluidized bed columns with different bed heights and flow rates were then carried out in up-flow mode to determine the effects of operational conditions on organic removal efficiency. Liquid chromatography–organic carbon detection (LC–OCD) was used to determine the removal of different organic fractions by GAC and purolite A502PS fluidized bed columns. The regeneration and reuse of exhausted purolite A502PS that had treated RO feed was also evaluated. In this study, Langmuir, Freundlich, Homogeneous surface diffusion models (HSDM) and plug flow model were applied to determine the equilibrium and kinetics behaviour of both GAC and purolite A502PS.

2. Materials and methods

2.1. Materials

2.1.1. Wastewater

Actual RO feed collected from the water reclamation plant in Sydney Olympic Park, Australia was used as the water source. The physico-chemical characteristics of the RO feed are summarized in Table 1.

Table 1
Physico-chemical characteristics of RO feed.

Parameters	Unit	RO feed
pH		6.8–7.6
Conductivity	μS/cm	680–1120
DOC	mg/L	3.6–7.7
F^-	mg/L	0.7–1.1
Cl^-	mg/L	132–150
NO_3^-	mg/L	4.5–6.1
PO_4^{+3}	mg/L	1.8–2.4
SO_4^{-2}	mg/L	49–51
Na^+	mg/L	86–90
K^+	mg/L	15–21
Ca^{+2}	mg/L	21–23.2
Mg^{+2}	mg/L	10–11.5

2.1.2. GAC and purolite A502PS

The characteristics of GAC and purolite A502PS used in this study are provided in Table 2.

2.2. Experimental methods

2.2.1. Adsorption equilibrium

Adsorption equilibrium studies were conducted with GAC and purolite A502PS separately. Different doses of GAC (0.1–1.2 g/L) and purolite A502PS (0.1–5 g/L) were added into 200 mL conical flasks containing RO feed water. The conical flasks were placed on a Ratek Platform Mixer at 110 rpm and shaken continuously for 24 h. Following this the samples were filtered through a 0.45 μm filter and the DOC was measured in a Multi N/C 2000 analyser.

2.2.2. Adsorption kinetics

Kinetics experiments were conducted to determine the DOC adsorption rate of GAC and purolite A502PS. A fixed amount of GAC (1 g/L) and purolite A502PS (1 g/L) were separately added into flasks containing 200 mL of RO feed and then placed on the Ratek Platform Mixer at 110 rpm. Samples were collected at different times, ranging from 5 min to 420 min and they were filtered through a 0.45 μm filter before DOC measurement.

2.2.3. Fluidized bed contactor

The schematic diagram of the experimental set-up is presented in Fig. 1. Columns with 2 cm diameter and a vertical length of 1 m were used. The feed water passage was maintained at a constant flow rate in the up-flow mode. During the experiment, fluidized bed heights of packing media were measured using a simple measuring tape/stick.

DOC removal from RO feed by GAC and purolite A502PS fluidized beds were studied separately at the different experimental conditions listed below.

2.3. Experiment with GAC

1. Doses of GAC: 5 g, 10 g, and 15 g.
2. Fluidization velocities: 5.7 and 11.4 m/h.

Table 2
Characteristics of purolite A502PS and GAC.

	Purolite A502PS	GAC
Type/structure	Macroporous polystyrene crosslinked with divinylbenzene	Coal based premium grade (MDW4050CB)
Exchange/adsorption capacity	0.85 eq/l min (Cl^- form)	Iodine #1000 mg/g
Moisture content	66–72%	2% max
Particle size	425–600 μm	425–600 μm
Surface area	21 m^2/g	1000 ± 50 m^2/g

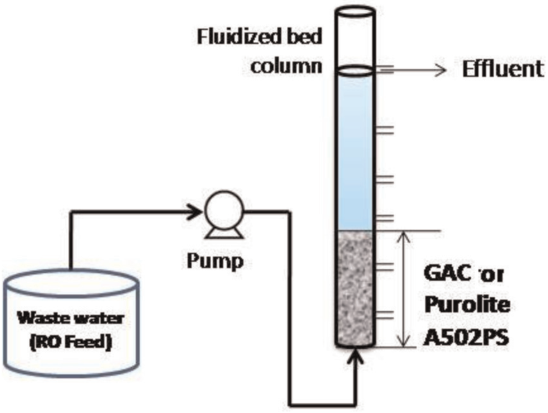

Fig. 1. Schematic diagram of the experimental setup of fluidized bed columns.

2.4. Experiment with purolite A502PS

1. Doses of purolite A502PS: 5 g, 15 g, and 30 g.
2. Fluidization velocities: 5.7 and 11.4 m/h.
3. Using fresh and regenerated purolite resins.

2.5. Analytical methods

2.5.1. Measurement of DOC

Measured using a Multi N/C2000 TOC analyser after filtering samples through 0.45 μm was used.

2.5.2. Liquid chromatography-organic carbon detection (LC–OCD)

LC–OCD Model 8 developed by DOC Labor, Dr Huber (Germany) was used. This system employs size-exclusion chromatography to separate classes of dissolved organic materials present in wastewater based on their molecular weights before measuring them via catalysed UV oxidation.

2.5.3. Analysis of sulfate and nitrate

Was measured using Metrohm ion chromatograph (model 790 Personal IC) equipped with an auto sampler and conductivity cell detector.

2.6. Mathematical modelling

The Langmuir, Freundlich, and Sips models were used for an equilibrium study of GAC and purolite A502PS with RO feed.

The Langmuir equation assumes that there is no interaction between the sorbate molecules and that the sorption is localized in a monolayer. It also assumes that once a sorbate molecule occupies a site, no further sorption can take place at that site. Theoretically, therefore, a saturation value is reached, beyond which no further sorption occurs [20]. The Langmuir isotherm is defined by Eq. (1):

$$q_e = \frac{q_m \times b \times C_e}{1 + b \times C_e} \tag{1}$$

where: q_e is the amount of organic adsorbed per gram of the adsorbent at equilibrium (mg/g); q_m is the saturated maximum monolayer adsorption capacity (mg/g); b is Langmuir adsorption constants related to the binding energy of adsorption (L/mg); and C_e is the equilibrium concentration (mg/L).

Adsorption of natural organic matter by anion exchange resins is expected to be heterogeneous [21,22]. Therefore the Freundlich model can be used for adsorption by purolite A502PS. The Freundlich isotherm is an empirical equation developed based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites. Here the relationship between the amount of DOC adsorbed on the purolite A502PS and the DOC left in the RO feed can be modelled by Eq. (2):

$$q_e = K_F \times C_e^{1/n} \tag{2}$$

where K_F is a Freundlich constant indicative of the adsorption capacity of the resin, n is an experimental constant indicative of the adsorption intensity of the resin, and C_e is the equilibrium concentration of DOC in the RO feed.

The Sips model is a different empirical model representing equilibrium adsorption data. This isotherm model has features that are common to both the Langmuir and Freundlich isotherm models. As a combination of the Langmuir and Freundlich isotherm models, the Sips model contains three parameters: q_m, b and n which can be evaluated by fitting the experimental data. For single solute equilibrium data, the Sips adsorption isotherm model can be written as follows:

$$q_e = \frac{q_m (bC_e)^{1/n}}{1 + (bC_e)^{1/n}} \tag{3}$$

The homogeneous surface diffusion model (HSDM) used to calculate the mass balance of dissolved organic matter inside a spherical porous particle was applied to analyse adsorption kinetics of both the GAC and purolite A502PS. The HSDM consists of a three-step process [23]: (i) the adsorbate diffuses through a stagnant liquid film layer surrounding the adsorbent particle; (ii) the adsorbate adsorbs from the liquid phase onto the outer surface of the adsorbent particle; and (iii) the adsorbate diffuses along the inner surface of the adsorbent particles until it reaches its adsorption site. The equations of HSDM are as follows:

$$\frac{\partial q_t}{\partial t} = D_s \left(\frac{\partial^2 q_t}{\partial r^2} + \frac{2}{r} \frac{\partial q_t}{\partial r} \right) \tag{4}$$

The above equation can be numerically solved using the following initial and boundary conditions: $t = 0$; $q_t = 0$

$$r = 0;\ \frac{\partial q}{\partial t} = 0 \tag{5}$$

$$r = r_p;\ D_s \rho_p \frac{\partial q_t}{\partial r} = K_f (C - C_s) \tag{6}$$

where q_t is the rate of change of surface concentration with time (t) at any radial distance (r) from the centre of the GAC or purolite A502PS particle during the adsorption/ion exchange process (mg/g); D_s is the surface diffusion coefficient which represents the rate of diffusion of the DOC along the surface of the GAC and purolite A502PS (m^2/s); K_f is the external mass transfer coefficient (m/s); ρ_p is the apparent density of the GAC and purolite A502PS (kg/m^3); C is the bulk phase concentration, mg/L; and C_s is the concentration on the external surface of adsorbent particles (mg/L).

In order to solve the HSDM equation, the orthogonal collocation method (OCM) and the variable coefficient ordinary differential equation solver (VODE) were used [24,25]. The Nelder–Mead simplex method was employed to extract the optimized parameters (D_s and K_f) [17,26].

3. Results and discussion

3.1. Batch studies

3.1.1. Adsorption – ion exchange equilibrium

Adsorption equilibrium experiments were conducted to predict the adsorption and exchange capacity of GAC and purolite A502PS

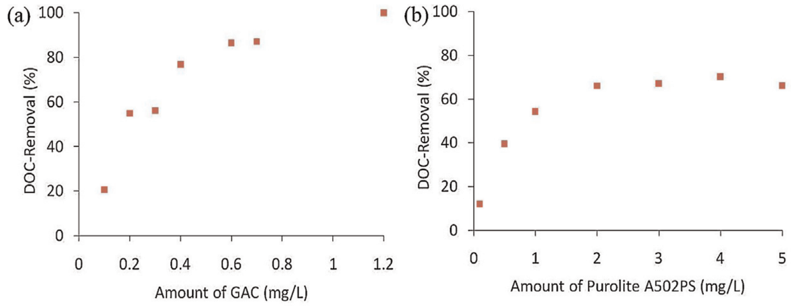

Fig. 2. Effect of GAC and purolite A502PS amount on removal of DOC from RO feed (initial DOC concentration with GAC and purolite experiments: 5–5.2 mg/L).

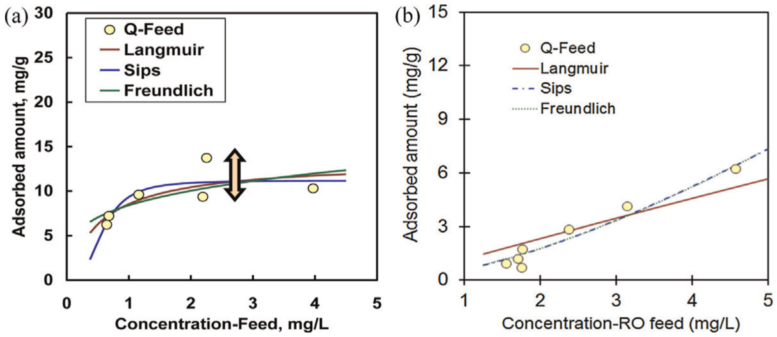

Fig. 3. Modelling of adsorption and ion-exchange equilibrium for (a) GAC and (b) purolite A502PS with RO feed (initial DOC concentration: 5–5.2 mg/L).

resin with RO feed. Fig. 2 illustrates the removal efficiency of DOC as a function of GAC and purolite A502PS dosage.

As expected, an increase in adsorbent or resin dose improved the removal efficiency of DOC as there was a larger surface area and more ion-exchange sites to adsorb or exchange organic electrolytes. GAC was able to remove DOC better than purolite A502PS. DOC was nearly completely removed (98%) at a GAC dose of 1.2 g/L whereas only 70.2% DOC removal was achieved using purolite A502PS dosage of 5 g/L.

The equilibrium results were then fitted with Langmuir, Sips and Freundlich isotherm equations. The adsorption curves predicted by these models and isotherm parameters are presented in Fig. 3 and Table 3, respectively.

The adsorption curves for purolite A502PS predicted by all of these models fitted the observed values well, and the correlation coefficients (r^2) for all isotherms were between 0.808 and 0.948. It can be seen that the Langmuir and Sips models yielded nearly similar values for DOC adsorption capacity (q_m) of GAC with RO feed. The maximum adsorption capacity calculated by Langmuir was 13.421 mg/g GAC.

K_F reflects the adsorption/exchange capacity of materials and for a given value of K_F, a higher value of n indicates a stronger solute affinity [21]. The results from the Freundlich isotherm (Table 3) indicate that the adsorption capacity of GAC with RO feed was much higher that the exchange capacity of purolite A502PS resin with RO feed. This can be partly explained by GAC's high surface area which was nearly 50 times larger than that of purolite A502PS (Table 2). In addition the RO feed consists of a high concentration of inorganic anions (Table 1) which have a high affinity with ion exchange resin. Matulionytė et al. [27] used purolite A500, an earlier version of purolite A502PS, to remove various components from fixing rinse water. They found that purolite A500 was good at adsorbing $S_2O_3{}^{-2}$ (4.34 meq), CH3COO$^-$ (0.69 meq), and $SO_4{}^{2-}$ (0.48 meq). In a similar manner, the strong competition of other anions at high concentrations in RO feed reduced the amount of DOC removed by purolite A502PS.

The $1/n$ value of the adsorption equilibrium of GAC with RO feed was 0.256, and much lower than 1, indicating that the isotherm shapes were concave curvilinear (favourable) [21]. In contrast, the $1/n$ of the adsorption equilibrium of purolite A502PS with RO feed was 1.55 which confirms that the isotherm is of type III and therefore unfavourable.

Table 3
Isotherm model parameters for GAC and purolite A502PS.

Parameters		GAC	Purolite A502PS
Langmuir	q_m	13.421	122.76
	b	1.748	9.679E-3
	r^2	0.594	0.808
–			
Freudlich	K_F	8.404	0.607
	n	3.9	0.644
	r^2	0.490	0.946
–			
Sips	q_m	11.185	102.16
	b	5.054	5.794E-3
	n	0.331	0.621
	r^2	0.679	0.948

4. Kinetics experiment

The kinetics results of GAC and purolite A502PS were fitted with the HSDM model and the results are presented in Fig. 4, while the parameters of the model are shown in Table 4. The experimental results reveal that DOC in RO feed was quickly adsorbed by GAC and purolite A502PS within the first 300 min and then remained constant. In both cases, until becoming constant, the available sites in the GAC surface for adsorption and available exchange sites in the purolite A502PS were abundant.

The results show that the fit between the simulation curve the experimental values was good. The external mass transfer coefficient K_f for DOC adsorbed by GAC in RO feed was higher

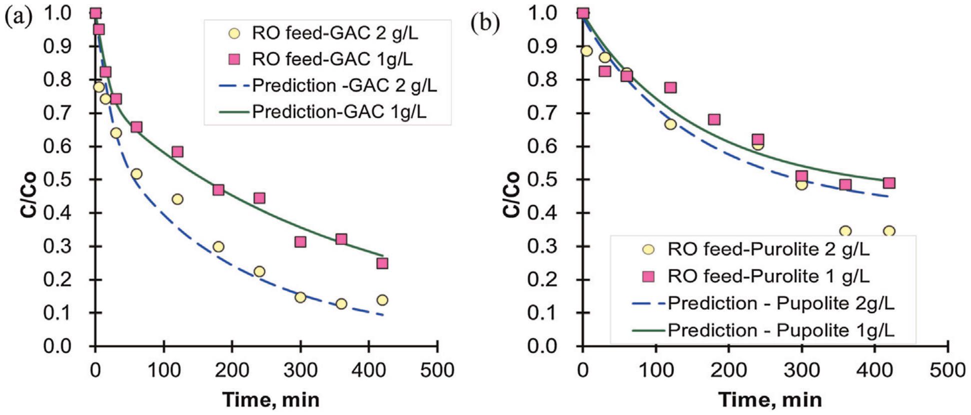

Fig. 4. Prediction of adsorption kinetics of (a) GAC and (b) purolite A502PS with RO feed by the HSDM model (initial DOC of RO feed was 4.5–5.8 mg/L and 3.6–7.7 for GAC and purolite A502PS respectively).

Table 4
The mass transfer coefficients of GAC and purolite A502PS with RO feed.

	GAC		Purolite A502PS	
	1 g/L	2 g/L	1 g/L	2 g/L
Initial conc (mg/L)	4.5	5.8	7.7	3.6
K_f (m/s)	12.92E-06	8.50E-06	1.59E-06	3.01E-06
D_s (m^2/s)	2.12E-14	2.25E-14	2.80E-13	2.01E-13

than that for purolite A502PS. K_f is dependent on agitation speed and the higher density of purolite A502PS compared to GAC could explain its lower value of K_f.

The results show that the surface diffusion D_s is a function of the equilibrium concentration C_e. The relationship of solid diffusion D_s and equilibrium concentration C_e for GAC and purolite A502PS can be expressed as Eqs. (7) and (8), respectively:

$$D_s = 1.739\text{E} - 14e^{4.401\text{E}-0.2C_e} \quad (7)$$

$$D_s = 1.498\text{E} - 13e^{8.115\text{E}-0.2C_e} \quad (8)$$

5. Fluidized bed experiments

5.1. Effect of GAC doses

5.1.1. Fluidized bed with GAC

Firstly, the effect of the GAC doses on DOC removal efficiency was studied. Fig. 5 shows the DOC removal efficiency of the GAC fluidized bed column for different doses of GAC. In this study, 5 g, 10 g and 15 g of GAC were packed into three separate columns corresponding to 3 cm, 7 cm and 10 cm bed height and the fluidization velocity was retained at 5.7 m/h.

To properly analyze the removal behavior of DOC in the column, a "plug flow model" was employed. The mass balance used here was coupled with the adsorption isotherm equation and HSDM. To derive the model, the following assumptions were used: (1) the system followed plug flow conditions without axial dispersion, and (2) the adsorbents in the bed are uniformly distributed. The equations of this model are as follows:

$$\frac{\partial C}{\partial t} = -\frac{v}{\varepsilon_r}\frac{\partial C}{\partial z} - \frac{(1-\varepsilon_r)}{\varepsilon_r} \times \rho_p \times \frac{\partial q}{\partial t} \quad (9)$$

$$\varepsilon_r = 1 - (1-\varepsilon_{mf}) \times \left(\frac{L_{mf}}{L_f}\right) \quad (10)$$

where L_{mf} is the height of the initial fixed bed, L_f is the height of the fluidized bed, ε_r is a voidage of the fluidized bed, and ε_{mf} is a voidage of the fixed bed. $\partial q_t/\partial t$is determined by Eqs. (4)–(6). Here D_s was determined from batch kinetics and K_f was determined using the Nelder–Mead simplex method [17,26].

The bed height before and after fluidization, detention time and model parameters are presented in Table 5. Fig. 6 shows the model prediction for removing organic matter from the RO feed using the plug flow model. Here the up-flow fluidization velocity and detention time were calculated by Eqs. (11) and (12).

$$v = \frac{Q}{\pi r^2} \quad (11)$$

$$t = \frac{L_f}{v} \times 60 \quad (12)$$

where v is the upflow fluidization velocity (m/h), t is the detention time (min), Q is the flow rate (m^3/h), and r is the radius of the fluidized column (m).

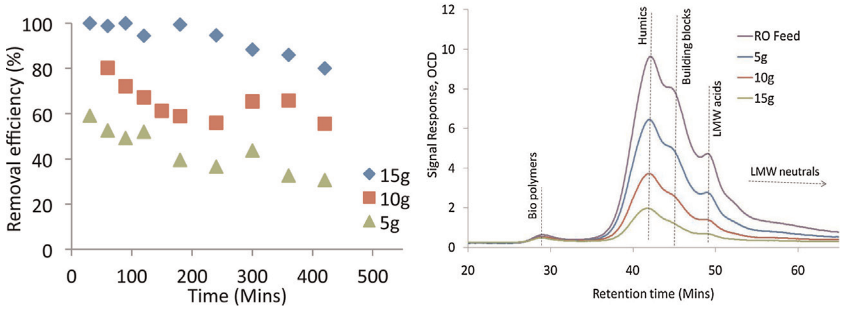

Fig. 5. Effect of GAC doses on the removal of DOC by fluidised bed column (a) DOC removal efficiency (b) organic fraction removal (5 g, 10 g and 15 g of GAC; initial DOC of RO feed was 4.7 mg/L, fluidization velocity: 5.7 m/h).

Table 5
Bed height after and before the fluidization, detention time, K_f, D_s of GAC fluidized contactor at different doses.

GAC dose (g)	Bed height before fluidization (cm)	Bed height after fluidization (cm)	Detention time (min)	ε_{mf}	K_f (m/s)	D_s (m^2/s)
5	3	4	0.4	0.45	6.42E-6	2.14E-14
10	7	8.5	0.9	0.45	6.96E-6	2.14E-14
15	10	12.5	1.3	0.45	7.75E-6	2.14E-14

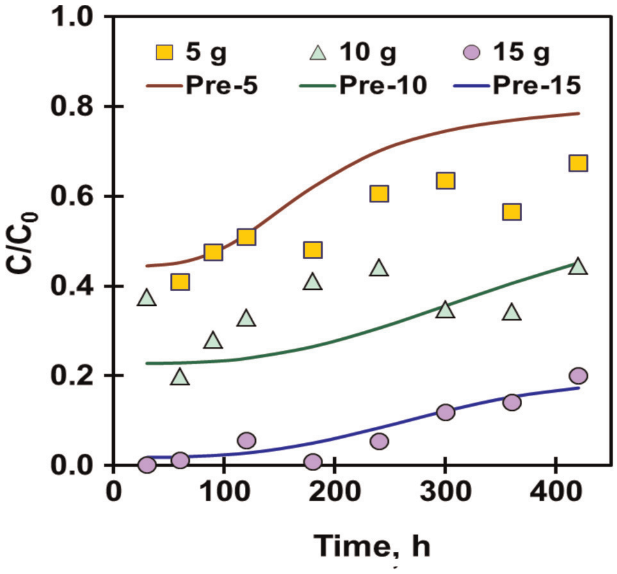

Fig. 6. Fluidized bed simulation with different doses of GAC (5 g, 10 g and 15 g of GAC; initial DOC of RO feed was 4.7 mg/L, fluidization velocity: 5.7 m/h).

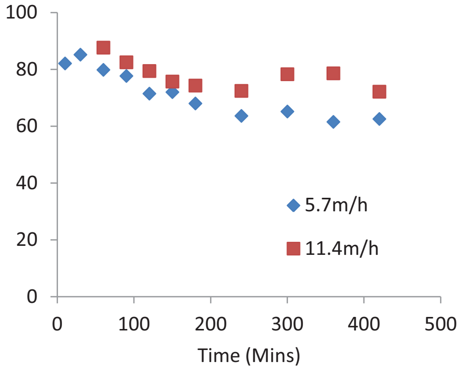

Fig. 7. Effect of fluidization velocity on the organic removal by fluidised bed column (initial DOC of RO feed: 4.7 and 7.5 mg/L for filtration velocity of 5.7 and 11.4 m/h; amount of GAC 10 g).

As expected, more than 80% of DOC was removed by the larger amount of GAC (15 g) over the first 7 h of the experiment. The smaller doses of GAC (10 g and 5 g) reduced DOC removal efficiency to 60% and 30% after 7 h, respectively. The rapid decline in DOC removal efficiency using a small amount of GAC can be explained by the small surface area and a shorter detention time.

The LC–OCD result shows that RO feed water contains mostly hydrophilic compounds (74.7%). This result is in agreement with Jarusutthirak et al. [3], who found higher concentration of hydrophillic compounds in secondary effluents. These compounds was further classified as biopolymers (1.6%), humics (42.2%), building blocks (16.2%), and low molecular weight (LMW) (14.7%). Here, biopolymers include polysaccharides and proteins; building blocks include hydrolysates of humic substances; LMW neutrals and amphiphilics (slightly hydrophobic compounds) include sugars, alcohols, aldehydes, ketones and amino acids [7]. The removal efficiency of different organic fractions is presented in Table 6. As expected, the increase in amount of GAC in the column increased the adsorption efficiency of all organic fractions. Hydrophilic compounds were more effectively removed than hydrophobic substances. With 15 g of GAC in the column 82.1% of hydropillic and 77.5% hydrophobic compounds were removed. Gur-Reznik et al. [10] also reported similar rejection rates for hydrophobic and hydropillic fractions when removing organics from tertiary wastewater effluent by GAC column. The medium molecular weight (MW) compounds such as humics (~1000 Da) and building blocks (300–500 Da) were adsorbed effectively (more than 85%) by the GAC column. Biopolymer, a high molecular weight substances (about 20,000 Da), was barely removed by the GAC column (Fig. 5b). However, biopolymers part only accounted for a very small part of the RO feed.

6. Effect of fluidization velocities

Fluidization velocity and detention time are other factors that could affect the removal of DOC. As such two different fluidization velocities, 5.7 m/h and 11.4 m/h (corresponding to detention times of 0.9 min and 0.6 min, respectively), were selected and applied in fluidized bed columns which contained 10 g GAC. The results show that there was only a minor difference in removing organic matter between two fluidization velocities (Fig. 7).

The plug flow model simulation of the organic material removal from the RO feed by the GAC column was good (Fig. 8). The related values of the D_s and K_f coefficients are presented in Table 7. The increase of fluidization velocity increased the external mass-transfer coefficients K_f. This can be explained by the adsorbent's faster movement in the column and this led to more shear at the particle surface and reduced the boundary layer film.

Since higher concentrations (7.5 mg/L) of RO feed were used for flow rate of 11.4 m/h the D_s value for the low rate was consequently higher than that for a flow rate of 5.7 m/h.

6.1. Long-term fluidized bed experiments with GAC

Long-term fluidized bed experiments were conducted with GAC dose of 30 g at two different fluidization velocities of 5.7 and 11.4 m/h (Fig. 9). Initially both filtration velocities almost completely removed the DOC and then the removal of organics gradually

Table 6
The effect of GAC doses on the removal of organic fractions.

GAC amount (g)	Hydrophobic (%)	Hydrophilic (%)	Hydrophilic (%)			
			Bio polymers	Humics	Builing blocks	LMWs
5	43.9	35.5	17.8	41.3	26.4	30.7
10	50.7	61.3	32.2	68.1	66.8	39.2
15	77.5	82.1	50.0	85.3	85.7	72.3

Table 7
Mass transfer coefficients in RO feed at different fluidization velocities – GAC.

Fluidization velocity (m/h)	Bed height before fluidization (cm)	Bed height after fluidization (cm)	Detention time (min)	ε_{mf}	K_f (m/s)	D_s (m^2/s)
5.7	7	8.5	0.9	0.45	9.04E-5	2.14E-14
11.4	7	11.5	0.6	0.45	19.88E-5	2.42E-14

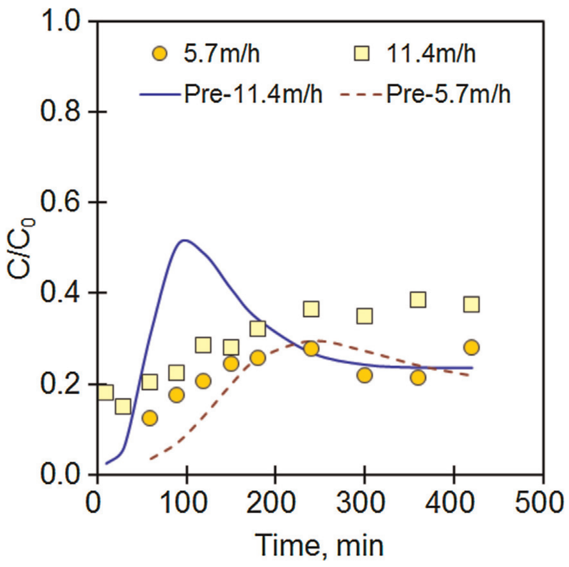

Fig. 8. Fluidized bed model simulation with different fluidization velocities (initial DOC of RO feed: 4.7 and 7.5 mg/L for filtration velocity of 5.7 and 11.4 m/h; GAC dose = 10 g).

reduced to 20% after 325 h and 175 h respectively at 5.7 and 11.4 m/h. Doubling the filtration velocity means that twice the amount of water passed through the columns. This caused the packed GAC to exhaust in half the contact time.

6.2. Fluidized bed with purolite A502PS

6.2.1. Effect of purolite A502PS dose

The effect of purolite A502PS dose on the removal of organics in the fluidized bed was also studied. Fig. 10 clearly shows that a higher dose of purolite A502PS resulted in more DOC being removed. The column packed with 30 g purolite A502PS could remove around 60–80% DOC over 7 h. This removal efficiency was a little less than previous results as reported by Ahmad et al. [17], who found that about 80% of DOC was removed from synthetic wastewater by a 28 g of purolite A500PS fluidized bed column over 8 h. Their experiment was carried out with a detention time of 3 min and wastewater with 10 mg DOC/L. The smaller amount of purolite A502PS in the fluidized bed column led to much less DOC removal (less than 27% and 5% DOC removal from 15 g and 5 g purolite A502PS, respectively).

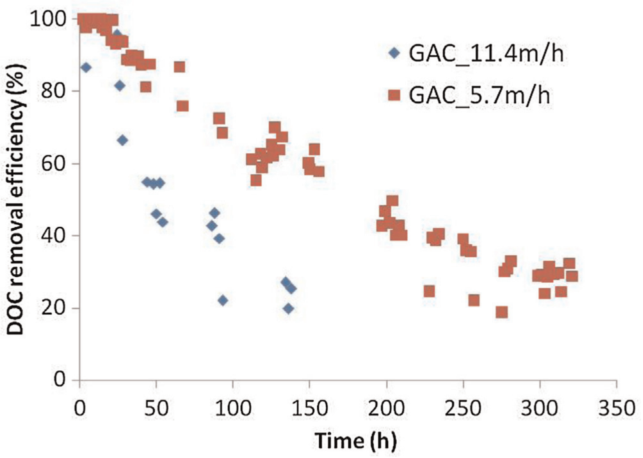

Fig. 9. DOC removal by GAC fluidised bed in long term study (Initial DOC of RO feed: 4.0–6.0 mg/L, filtration velocities of 5.7 and 11.4 m/h; GAC dose = 30 g).

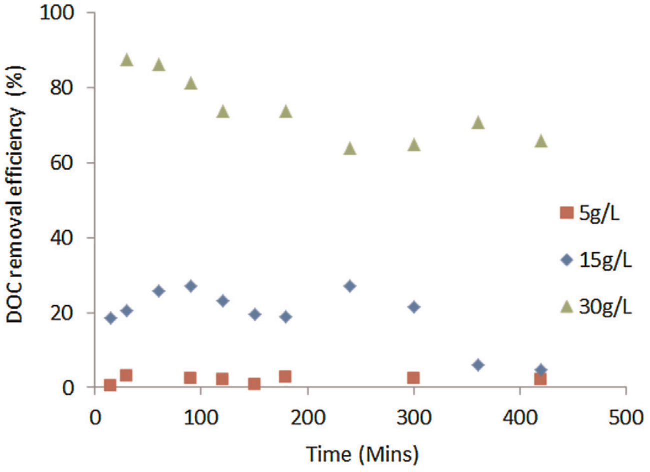

Fig. 10. DOC removal efficiency of purolite A502PS with different doses (initial DOC = 4.2–4.7 mg/L, fluidised velocity = 5.7 m/h).

The plug flow model was also employed and it was able to predict the DOC removal of purolite A502PS fluidized column with RO feed. The prediction curve and model parameters are presented in Fig. 11 and Table 8 respectively.

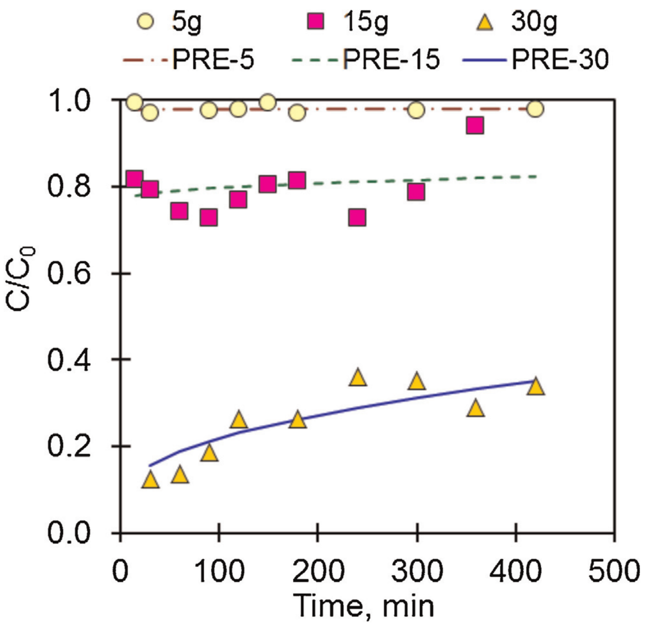

Fig. 11. Fluidized bed simulation for different doses of purolite A502PS.

Table 8
Bed height after and before the fluidization, detention time, K_f, D_s of purolite A502PS contactor fluidized contactor at different doses.

Purolite A502PS dose (g)	Bed height (cm)		Detention time (min)	K_f (m/s)	D_s (m^2/s)
	Before fluidization	After fluidization			
5	2.5	3	0.3	9.202E-8	2.110E-13
15	7.5	10.5	1.1	4.836E-7	2.110E-13
30	15	22	2.3	2.145E-5	2.194E-13

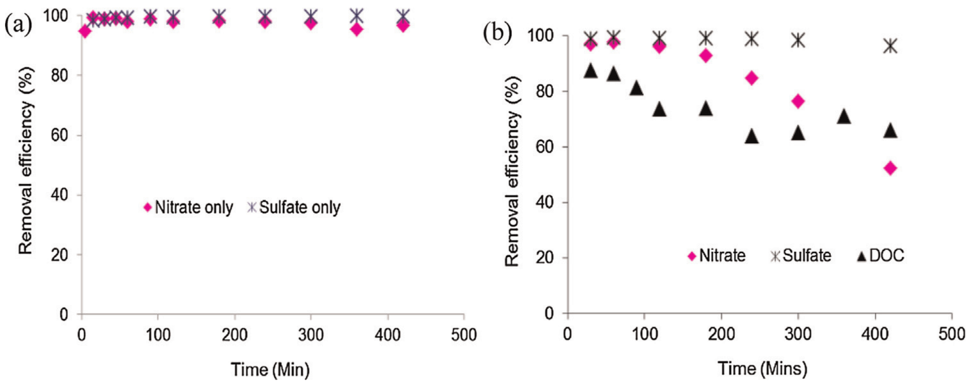

Fig. 12. Removal efficiency of purolite A502PS with nitrate and sulphate (a) without the presence of EfOM and (b) with the presence of EfOM (NO_3^-: 5 mg/L, SO_4^{2-}: 50 mg/L, purolite amount: 30 g, flow rate: 5.7 m/h).

Similar to our previous observation with GAC, a higher K_f value occurs when a larger dose of purolite A502PS was used. It is interesting to note that purolite A502PS was heavier than GAC. As such, its movement in the fluidized column was less than GAC in the same fluidized velocity. This led to bigger boundary layer film and as such the K_f for the purolite A502PS fluidized bed was smaller than that of GAC. The slight difference in initial concentration of RO feed led to little difference in the values of D_s.

Purolite A502PS also has very high affinity towards sulfate and nitrate. In the fluidised bed study with synthetic water containing only sulphate or nitrate, purolite A502PS could remove more than 95% of these components during a 7 h experiment (Fig. 12a). The removal efficiency of sulphate and nitrate were also higher than 94% and 88% in case of water containing both sulphate and nitrate. Here, the experimental conditions were similar to that of RO feed water (NO_3^-: 5 mg/L, SO_4^{2-}: 50 mg/L, purolite amount: 30 g, flow rate: 5.7 m/h). The presence of EfOM in the RO feed did not affect the removal ability of purolite A502PS with sulphate. However, similar to the DOC removal efficiency, the removal of nitrate reduced remarkably (Fig. 12b). It shows that purolite A502PS has excellent exchange capacity with sulfate and there is a strong competition between nitrate and DOC in exchanging with purolite A502PS.

Higher DOC removal efficiency (more than 80% DOC consistently in 8 h) was observed by purolite A500 (a previous version of purolite A502PS) with synthetic wastewater [17]. The reduction of DOC removal efficiency with RO feed can be explained by the competition of other anions such as sulphate and nitrate which were present in higher concentrations in RO feed (50 mg/L sulphate and 5 mg/L nitrate compared to only 15 mg/L sulphate and 1.5 mg/L nitrate in synthetic wastewater). The exchange mechanism of other anions with purolite A502PS is similar to that of DOC and this was explained clearly in our previous paper [28].

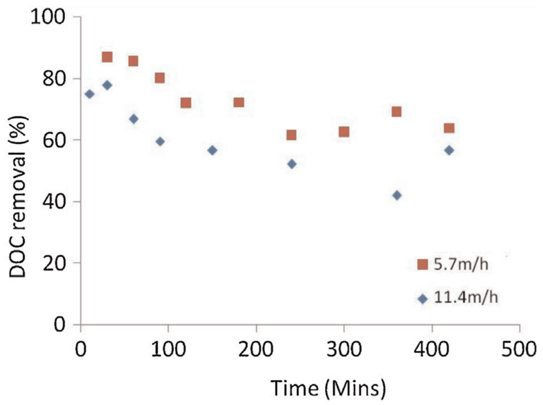

Fig. 13. DOC removal efficiency of purolite A502PS fluidized bed with different velocities 5.7 m/h and 11.4 m/h (initial DOC = 4.4 mg/L, purolite A502PS amount = 30 g).

7. Effect of fluidization velocities – purolite A502PS

As expected, a comparatively higher DOC removal efficiency was observed with high filtration velocity over 7 h of the experiment. Different velocities of 5.7 and 11.4 m/h (corresponding to detention times of 2.3 and 1.8 min) resulted in average removal efficiencies of 75% and 60%, respectively (see Fig. 13).

Table 9
Bed height after and before the fluidization, detention time, K_f, D_s of purolite A502PS columns at different fluidization velocities (initial concentration C_0: 4.4 mg/L).

Fluidization velocity (m/h)	Bed height (cm)		Detention time (min)	K_f (m/s)	D_s (m^2/s)
	Before fluidization	After fluidization			
5.7	15	22	2.3	1.687E-5	2.141 E-13
11.4	15	34	1.5	2.406E-5	2.141 E-13

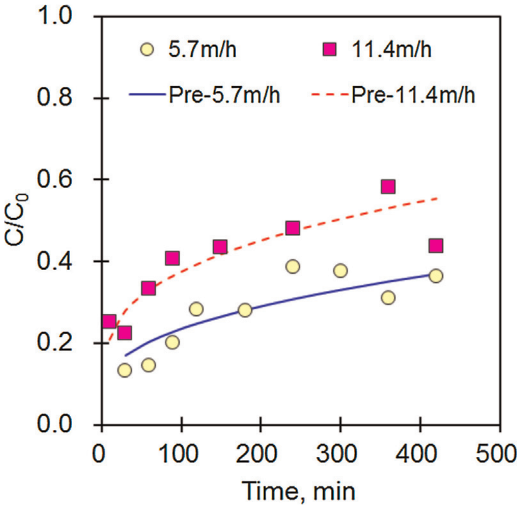

Fig. 14. Model simulation with different velocities of purolite A502PS fluidized bed.

The values of the model parameters (D_s and K_f) and prediction using the plug flow model are presented in Table 9 and Fig. 14. As noted previously, the external mass-transfer coefficients K_f increased when fluidization velocity accelerated. In terms of fluidized velocity, both K_f and D_s by purolite A502PS column were found to be less than that of the GAC column.

The LC–OCD data further explains the removal of organic fractions. The velocity of 5.7 m/h removed DOC more efficiently than a velocity 11.4 m/h as the contact time was double in the lower filtration velocity. The removal of humics and building blocks varied from 63.3 to 73%, and were higher than that of biopolymers (50.7–57.1%). However the LMWs removal was less than 38% as LMW neutrals are uncharged compounds (Table 10). Compared to GAC, purolite A502PS is not observed to be effective in removing organic fractions.

7.1. Long-term fluidized bed experiment

Long-term fluidized bed experiments with purolite A502PS was also conducted at the same experimental conditions (amount 30 g at filtration velocities 5.7 m/h and 11.4 m/h) (Fig. 15). Purolite removed 80–75% of DOC initially and the removal efficiency gradually decreased. At a low filtration velocity of 5.7 m/h, DOC removal efficiency decreased from 80% to 40% in 325 hours while at a high filtration velocity the DOC reduced from 75% to 20% in 150 h.

8. Performance of fresh vs. regenerated purolite A502PS

The performance of fresh and regenerated purolite A502PS was examined to check the feasibility of reusing purolite A502PS after its saturation with DOC present in the RO feed. After the experiment 1 N NaCl was passed through the exhausted purolite A502PS column for 5 h and then it was rinsed with deionized water several times to remove any excess NaCl. After that the RO feed was passed through the regenerated column at the same velocity. The operational conditions of both fresh and regenerated purolite A502PS were similar. Fig. 16 illustrates the trend in DOC removal efficiency of fresh and regenerated material over a 7 h period. It is observed that the regenerated material still maintained good ion-exchange capacity and achieved DOC removal efficiency of approximately 60% while the fresh material achieved on average 70%. It suggests that exhausted purolite A502PS could be recovered and re-used in a cost effective manner.

Table 10
The effect of purolite flow rates on the removal of organic fractions.

Purolite A502PS velocity (m/h)	Hydrophobic (%)	Hydrophilic (%)	Hydrophilic (%)			
			Bio polymers	Humics	Builing blocks	LMWs
5.7	59.6	61.6	57.1	67.3	73.0	38.2
11.4	53.9	55.8	50.7	64.1	63.3	30.6

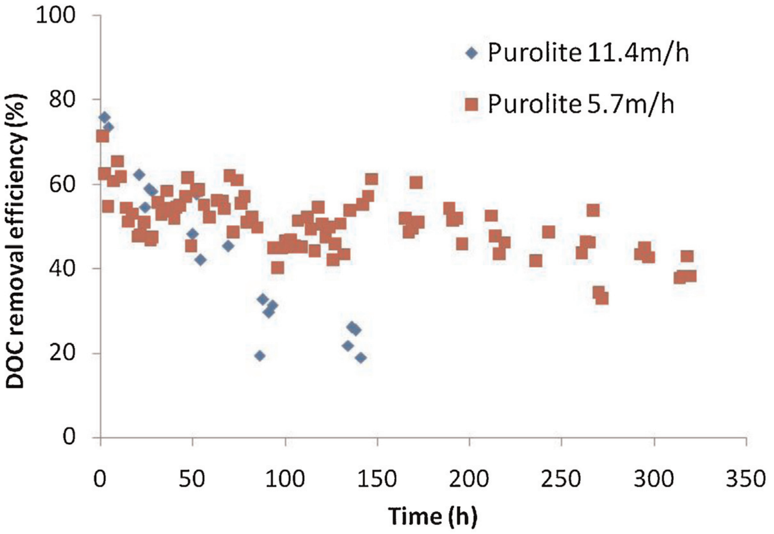

Fig. 15. DOC removal by purolite A502PS fluidised bed in long term study (initial DOC of RO feed: 3.9–5.7 mg/L, filtration velocities of 5.7 and 11.4 m/h; purolite amount = 30 g).

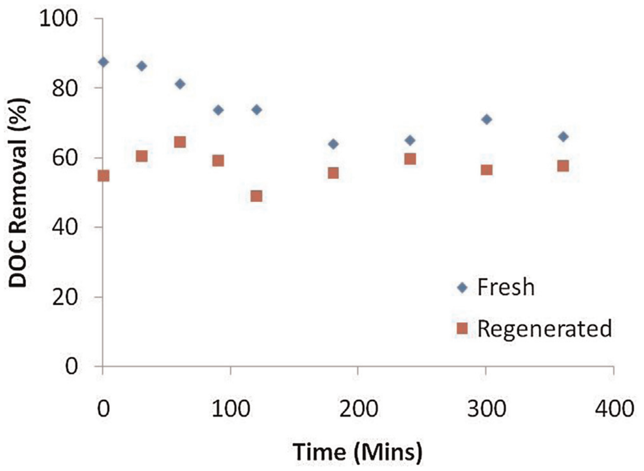

Fig. 16. DOC removal efficiency of fresh vs regenerated purolite A502PS (initial DOC of RO feed is 6.0 mg/L; fluidization velocity = 3.8 m/h; amount of purolite A502PS: 30 g).

9. Conclusions

Fluidized bed contactors packed with GAC and purolite A502PS are effective for a pre-treatment strategy of removing dissolved organic matter prior to RO. The removal efficiency of DOC strongly depends on operational conditions in which the bed height is more important than fluidization velocity. The performance of GAC and purolite A502PS columns in removing DOC can be modelled using the plug flow model. Results show that the performance of GAC is better than that of purolite A502PS in removing DOC from RO feed. The poorer ability of purolite A502PS may be due to its smaller surface area and the inference of other inorganic anions present in RO feed. Further, regenerated puroliteA502PS can be reused as it still maintains good ion-exchange capacity. In order to prevent scaling and other issues caused by inorganic dissolved ions, the purolite fluidization bed is good because it can remove anions from feed water better than GAC. A series of fluidized columns can provide better results in that they can effectively remove both organic matter and inorganic anions over a longer period of time.

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